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Supplementary Material A mechanistic understanding of surface Bi enrichment in dilute GaBi systems

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Ga₁₀₀ electronic density of states



Figure S1: Total electronic density of states for Ga_{100} nanocluster, exhibiting a pseudo-gap at the Fermi level and thus replicating Ga bulk-like electronic behavior.

Equilibration of seeding structures

Table S1: Average radial distribution function (RDF; left) and angular distribution function (ADF; right) for the Ga_{94} nanocluster (blue) and the Ga_{100} nanocluster (orange).



Seeding structures for long-timescale AIMD simulations

Table S2: Seeding structures for long–timescale simulations for Bi(c) systems. Bonds up to 3 Å are shown; Ga atoms are shown in grey and Bi atoms are shown in purple.



$\mathrm{Bi}(\mathrm{s})_0$	$\mathrm{Bi}(\mathrm{s})_1$	${ m Bi}({ m s})_2$
∳→ z	∳→ z	∳ → <i>z</i>
$Bi(s)_3$	$\operatorname{Bi}(s)_4$	$\operatorname{Bi}(s)_5$
\$→+z	ţ	\$ →→z
$Bi(s)_6$	$\operatorname{Bi}(s)_7$	$\operatorname{Bi}(s)_8$
		2 2 2 0
\$ → z	∮→z	ş n→z
Bi(s)9	$\operatorname{Bi}(s)_{10}$	

Table S3: Seeding structures for long-timescale simulations for Bi(s) systems. Bonds up to 3 Å are shown; Ga atoms are shown in gray and Bi atoms are shown in purple.

Lindemann index analysis of nanoclusters

System	Lindemann Index	System	Lindemann Index
$Bi(c)_0$	0.111	$Bi(s)_0$	0.123
$\operatorname{Bi}(c)_1$	0.084	$Bi(s)_1$	0.122
$\operatorname{Bi}(c)_2$	0.110	$Bi(s)_2$	0.113
$\operatorname{Bi}(c)_3$	0.119	$Bi(s)_3$	0.098
$\operatorname{Bi}(c)_4$	0.110	$Bi(s)_4$	0.120
$Bi(c)_5$	0.129	$Bi(s)_5$	0.111
$\operatorname{Bi}(c)_6$	0.092	$Bi(s)_6$	0.085
$\operatorname{Bi}(c)_7$	0.098	$\operatorname{Bi}(s)_7$	0.094
$\operatorname{Bi}(c)_8$	0.110	$Bi(s)_8$	0.091
$\operatorname{Bi}(c)_9$	0.112	$\operatorname{Bi}(s)_9$	0.110
$\operatorname{Bi}(c)_{10}$	0.111	$\operatorname{Bi}(s)_{10}$	0.107

Table S4: Lindemann indices for the different GaBi systems to ensure that they are all in the liquid state.



Figure S2: Diffusion of internal Bi overtime for the Bi(c) systems, with the average Ga surface being shown in blue and the average position of the internal Bi being shown as the red point. d is defined as the distance from the center of mass of the nanocluster.





Figure S3: Diffusion of internal Bi overtime for the Bi(s) systems, with the average Ga surface being shown in blue and the average position of the internal Bi being shown as the red point. d is defined as the distance from the center of mass of the nanocluster.

Linear regression for diffusion of internal Bi toward the surface

Table S5: Calculated linear regressions for the diffusion of the internal Bi atom. Linear regressions greater than 0.005 Å ps⁻¹ are classified as positive, between 0.005 and -0.005 Å ps⁻¹ are deemed to be statistically zero while linear regressions less than -0.005 Å ps⁻¹ are classified as negative.

System	Gradient	Classification
	$[\text{\AA ps}^{-1}]$	
$Bi(s)_0$	0.007	Positive
$Bi(s)_1$	0.006	Positive
$Bi(s)_2$	-0.001	Zero
$Bi(s)_3$	0.003	Zero
$Bi(s)_4$	0.028	Positive
$Bi(s)_5$	0.017	Positive
$Bi(s)_6$	0.000	Zero
$Bi(s)_7$	-0.003	Zero
$Bi(s)_8$	-0.001	Zero
$Bi(s)_9$	0.028	Positive
$Bi(s)_{10}$	0.015	Positive
$Bi(c)_0$	-0.017	Negative
$\operatorname{Bi}(c)_1$	-0.005	Negative
$\operatorname{Bi}(c)_2$	-0.003	Zero
$\operatorname{Bi}(c)_3$	0.000	Zero
$\operatorname{Bi}(c)_4$	-0.007	Negative
$\mathrm{Bi}(\mathrm{c})_5$	0.011	Positive
$\operatorname{Bi}(c)_6$	0.000	Zero
$\operatorname{Bi}(c)_7$	0.000	Zero
$\mathrm{Bi}(c)_8$	0.008	Positive
$\mathrm{Bi}(\mathrm{c})_9$	0.007	Positive
$\operatorname{Bi}(c)_{10}$	-0.006	Negative

Total mean square displacement



Figure S4: Total mean square displacement analyses for Bi(c) systems. Internal Bi is shown in red, average surface Bi is shown in blue and the average Ga is shown in green.





∆t[ps]

Figure S5: Total mean square displacement analyses for Bi(s) systems. Internal Bi is shown in red, average surface Bi is shown in blue and the average Ga is shown in green.

We note that as the number of surface Bi atoms increases, the total atomic mobility of all of the atoms in a system decreases (Figure S4, S5). We rationalize this using two arguments; firstly, surface atoms have a higher mobility than internal atoms¹ and secondly, that the lighter atoms (Ga) have a higher mobility than the heavier atoms (Bi).² Thus, in the cases where there are no surface Bi atoms capping the cluster, the surface Ga atoms have a high mobility. As the surface becomes capped by heavier Bi atoms, with a lower mobility, there is a decrease in the proportion of surface Ga atoms, therefore the mobility of all of the atoms in the cluster decreases.

Radial mean square displacement



Figure S6: Radial mean square displacement analyses for Bi(c) systems. Internal Bi is shown in red, average surface Bi is shown in blue and the average Ga is shown in green.





∆t[ps]

Figure S7: Radial mean square displacement analyses for Bi(s) systems. Internal Bi is shown in red, average surface Bi is shown in blue and the average Ga is shown in green.

Cone analysis

Figure S8 shows the necessity of only considering the atoms within the 45° cone when determining the lateral Ga network extension. If all atoms were considered, the local lateral extension of the Ga network around the internal Bi atom would be lost.



Figure S8: Lateral Ga network for $Bi(s)_9$ regime III, averaged over 20 ps, using only those atoms within the 45° cone (red) and all the atoms in the nanocluster (blue).

Ga-Bi interaction

As a further proxy for Ga-Bi interaction, additional to the ADF of the surface Bi atoms shown in the main text (Figure 2), we present here the pairwise distribution function (PDF) for the surface Bi atoms to Ga atoms.

In the case of $Bi(s)_4$ (Figure S9a) in regime III, the PDF is broader, indicating a less consistent interaction with the surrounding Ga atoms. In regime IV, there is a move to a shorter Ga-Bi interaction but more consistent peak. Finally, in regime V, there is a noticeable extension of the Ga-Bi PDF, however, this PDF is also a clear peak which shows consistent interaction with the Ga atoms.

In the case of $Bi(s)_9$ (Figure S9b), regime III shows a similar Ga-Bi interaction to that of $Bi(s)_4$, in that the Ga-Bi PDF exhibits a wider peak and thus there is a more irregular Ga-Bi interaction in this regime. In regimes IV and V there is a move to a more structured peak with a shorter Ga-Bi interaction. In regime V, there is no extension of the Ga-Bi interaction, as was observed for the $Bi(s)_4$ system however the $Bi(s)_9$ simulation was run for 100 ps whereas the $Bi(s)_4$ simulation was run for 200 ps.

Finally, for $Bi(c)_5$ (Figure S9c), the peak in regime I where the internal Bi is moving through the bulk Ga network is considerably more irregular, as exhibited by the broader peak, than that of regime VI.

In conclusion, we see a different pattern for the Ga-Bi interaction, characterised by a broader peak in the PDF, for those regimes in which we see Bi movement to the surface and a disruption of the Ga-Ga bonding network.



Figure S9: Pairwise distribution function between Ga and surface Bi atoms averaged over 20 ps for (a) $Bi(s)_4$, (b) $Bi(s)_9$ and (c) $Bi(c)_5$. Regime I is shown in red, regime II in green, regime III in blue, regime IV in magenta, regime V in cyan and regime VI in black.

Surface Bi patterning

Table S6: Surface Bi patterns forming with respect to time for Bi(c) systems. Bi atoms are shown in purple, Ga atoms are shown in green. Internal Bi is marked by yellow cross. Snapshots with less than 4 surface Bi atoms are not shown due to a lack of bond angles and patterning possibilities. Red lines highlight the pentagonal-like and chain surface Bi nanostructured patterns



Table S7: Surface Bi patterns forming with respect to time for $Bi(c)_5$ systems. Bi atoms are shown in purple, Ga atoms are shown in green. Internal Bi is marked by yellow cross. Red lines highlight the pentagonal-like surface Bi nanostructured patterns.



Table S8: Surface Bi patterns forming with respect to time for $Bi(s)_4$ systems. Bi atoms are shown in purple, Ga atoms are shown in green. Internal Bi is marked by yellow cross.

		$B_1(s)4$		
12 ps	32 ps	52 ps	72 ps	92 ps
L.	i.		L.	
112 ps	$132 \mathrm{\ ps}$	152 ps	172 ps	192 ps
L.	L.		L.	

Table S9: Surface Bi patterns forming with respect to time for Bi(s) systems. Bi atoms are shown in purple, Ga atoms are shown in green. Internal Bi is marked by yellow cross. Snapshots with less than 4 surface Bi atoms are not shown due to a lack of bond angles and patterning possibilities. Red lines highlight the pentagonal-like and chain surface Bi nanostructured patterned.







Count [arb. units]



Figure S10: Angular distribution function (ADF) analysis of the surface Bi atoms for Bi(c) systems. ADF analyses only include surface Bi atoms and are averaged over a 20 ps window.





Count [arb. units]



Figure S11: Angular distribution function analysis of the surface Bi atoms for Bi(s) systems. ADF analyses only include surface Bi atoms and are averaged over a 20 ps window.

Changes in electronic structure

Orbital projected density of states were used to investigate the details of the pseudo-gap of $Bi(s)_9$ at the Fermi level. No changes to the electronic structure were detected that could be responsible for or provide explanation of the migration of the internal Bi toward the surface (Figure S12, S13).



Figure S12: Orbital resolved density of states for $Bi(s)_4$ with respect to time





Density of states [states eV⁻¹]

Figure S13: Orbital resolved density of states for $Bi(s)_9$ with respect to time

Bonding structure analysis

Extensive investigations into possible bonding interactions were carried out because in all cases where movement of the internal Bi diffused toward the surface, the internal Bi diffused toward the surface Bi atoms. Furthermore, these analyses also probed the effect of having a larger (or smaller) surface Bi island. The analysis techniques used to probe the interaction between internal and surface Bi atoms were charge density differences and electron localization function (ELF) analysis.

We show, using ELF analysis of the $Bi(s)_9$ system (Figure S10) that there is no bonding interaction between the surface Bi island and the internal Bi as the internal Bi migrates toward the surface. We also include multiple reference plots in this analysis to show that there is nothing within the bonding structure of the $Bi(s)_9$ case that is unique when compared to Ga_{100} , $Bi(c)_9$ or with respect to time within the $Bi(s)_9$ system itself.

Electron localisation function analysis



Table S10: Electron localization function analysis for $Bi(s)_9$, with reference cases, at 4 ps and 40 ps. The ELF analysis shows there is no covalency between atoms within the nanocluster.

 $Bi(s)_9 (40 ps)$

Charge difference analysis

Using analysis of the charge distribution we probe the systems to check changes associated with the diffusion of the internal Bi to the surface. We are unable to use the charge distribution in its totality due to the dynamic nature of the clusters, which means that between two structures within a system difference in charge are unable to be distinguished from changes in structure. Instead, artificially manufactured structures must be analyzed.

The first is to compare the charge difference between the charge density of a structure taken from the AIMD simulation while still at temperature and compare it to the same structure that had been quenched to 0 K, allowing the effects of relaxation on the structure to be obtained. From Figure S11, it is evident that the effect of relaxation on the charge distribution of these clusters is small.

Table S11: Charge difference between single point and relaxed structures, with an isosurface value of 0.015.

The results from the ELF and charge density difference lead us to believe that there is no significant interaction between the internal Bi and the surface Bi and hence that the internal Bi is not being pulled toward the surface Bi island through a long-range bonding network or charge.

Changes in cluster distortion overtime

Next, the overall shape of the cluster was analyzed in detail. Due to the dynamic nature of the liquid cluster at temperature it was possible that distortion of the system could led to a perturbation required to initiate the surface-ward diffusion of the internal Bi.

Principle component analysis

The first analysis technique utilized to investigate cluster distortion over time was the principle component analysis (PCA) which is used to measure how spherical or distorted the nanocluster is. If distortion was present within the cluster, we would see that one of the axes (x, y or z) was significantly shorter or longer than the other one or two. From Figure S14 and S15, there are two important conclusions to take away. The first is that no cluster is significantly more distorted than any other cluster. That is to say that the cases in which the internal Bi diffuses toward the surface $(Bi(s)_4 \text{ and } Bi(s)_9)$ are not more or less distorted than any of the other clusters, in which little or no diffusion of the internal Bi toward the surface Bi is observed. The second conclusion is that within each system, there are no significant changes in the distortion of the cluster with respect to time. This means that at no point in time throughout the simulation was the cluster significantly more distorted than at any other time.

PCA

– Lx – Ly – Lz

Time [ps]

Figure S14: Principle component analysis of Bi(s) systems. L_x is shown in red, L_y is shown in blue and L_z is shown in green.

Lx Ly Lz

Time [ps]

Figure S15: Principle component analysis of Bi(c) systems. L_x is shown in red, L_y is shown in blue and L_z is shown in green.

References

- [1] Capelo, R., Leppert, L., Albuquerque, R., The concept of localised atomic mobility: Unraveling properties of nanoparticles. J. Phys. Chem. C 2014, 118, 21647–21654.
- [2] DiFoggio, R., Gomer, R., Diffusion of hydrogen and deuterium on the (110) plane of tungsten. *Phys. Rev. B* 1982, 25, 3490–3511.